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(54) **METHOD FOR FORMING FILM HAVING LOW RESISTANCE AND SHALLOW JUNCTION DEPTH**

(71) Applicant: **ASM IP Holding B.V.**, Almere (NL)

(72) Inventors: **Yosuke Kimura**, Hachioji (JP); **David de Roest**, Kessel-L (BE)

(73) Assignee: **ASM IP Holding B.V.**, Almere (NL)

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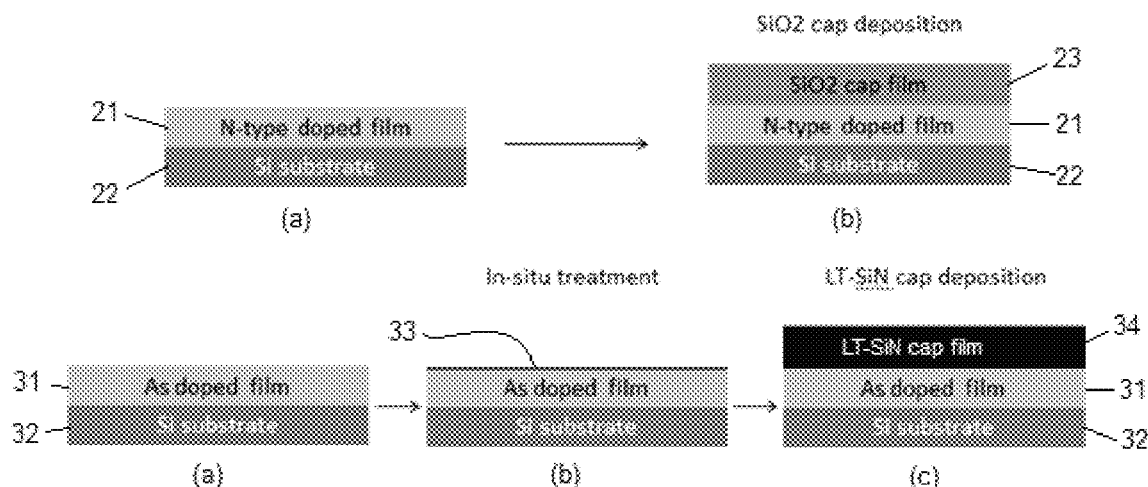
Primary Examiner — Timor Karimy

(74) *Attorney, Agent, or Firm* — Snell & Wilmer LLP

(57) **ABSTRACT**

A method for forming on a substrate a doped silicon oxide film with a cap film, includes: forming an arsenosilicate glass (ASG) film as an arsenic (As)-doped silicon oxide film on a substrate; continuously treating a surface of the ASG film with a treating gas constituted by Si, N, and H without excitation; and continuously forming a silicon nitride (SiN) film as a cap film on the treated surface of the ASG film.

18 Claims, 3 Drawing Sheets



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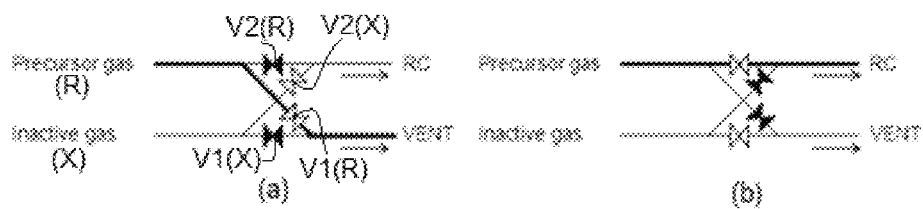
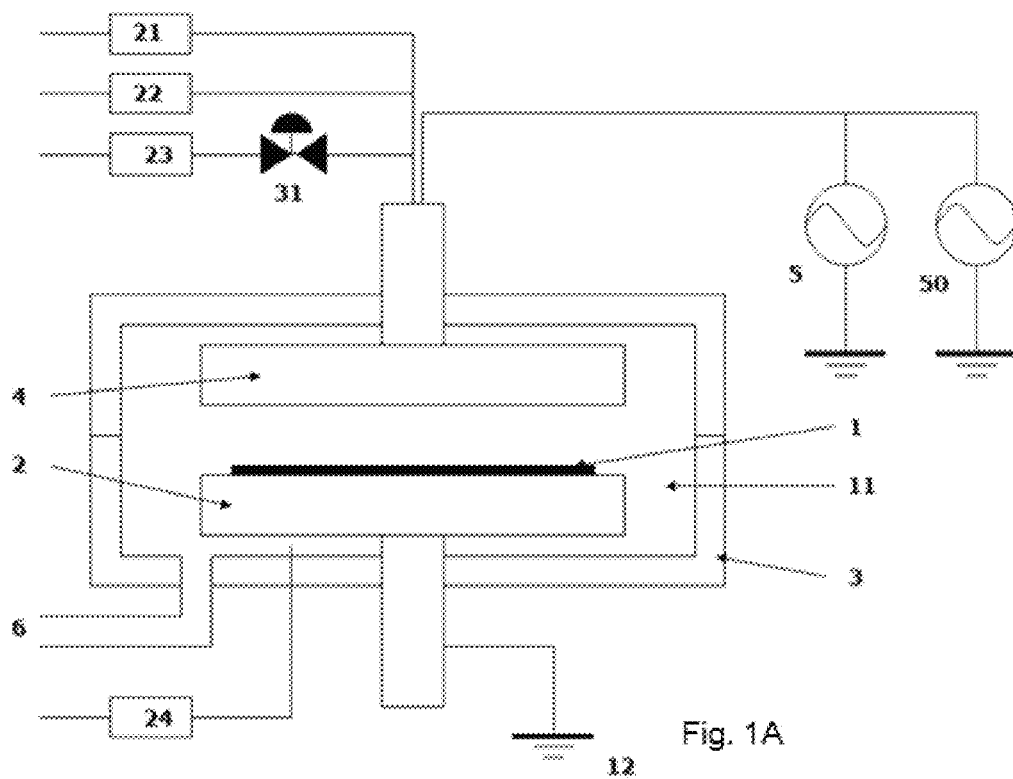


Fig. 1B

Fig. 2

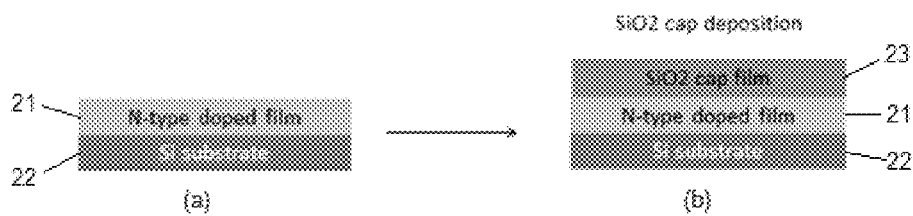


Fig. 3

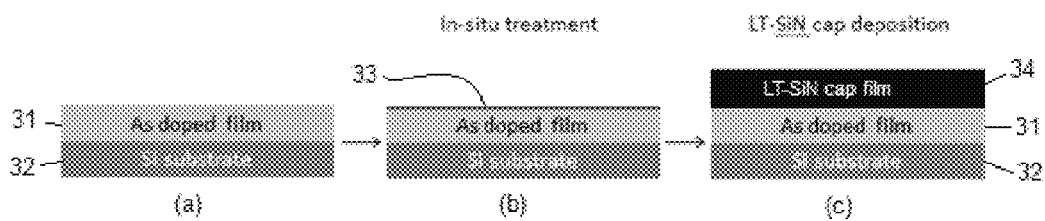


Fig. 4

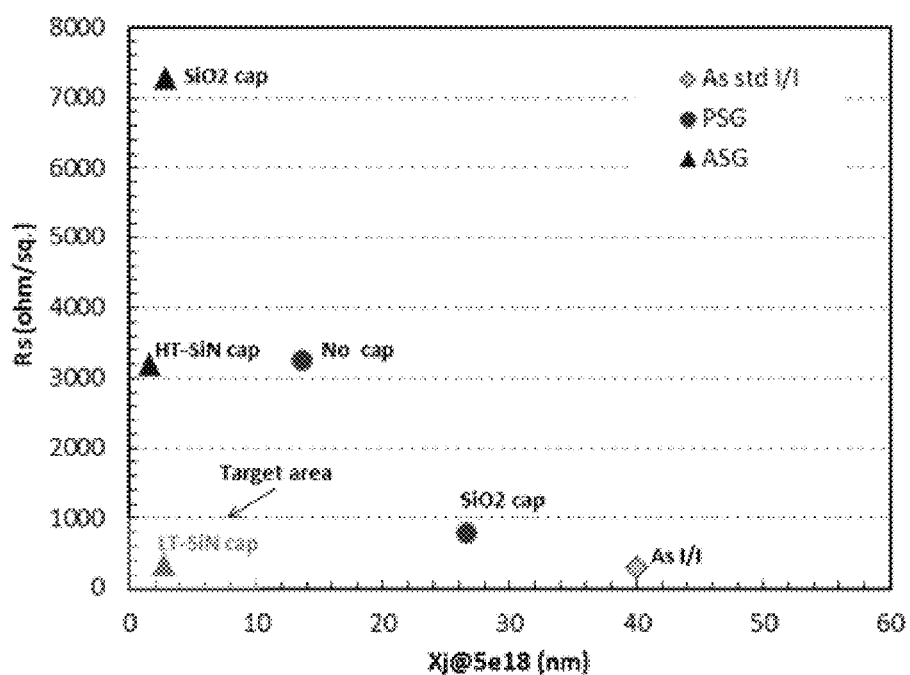
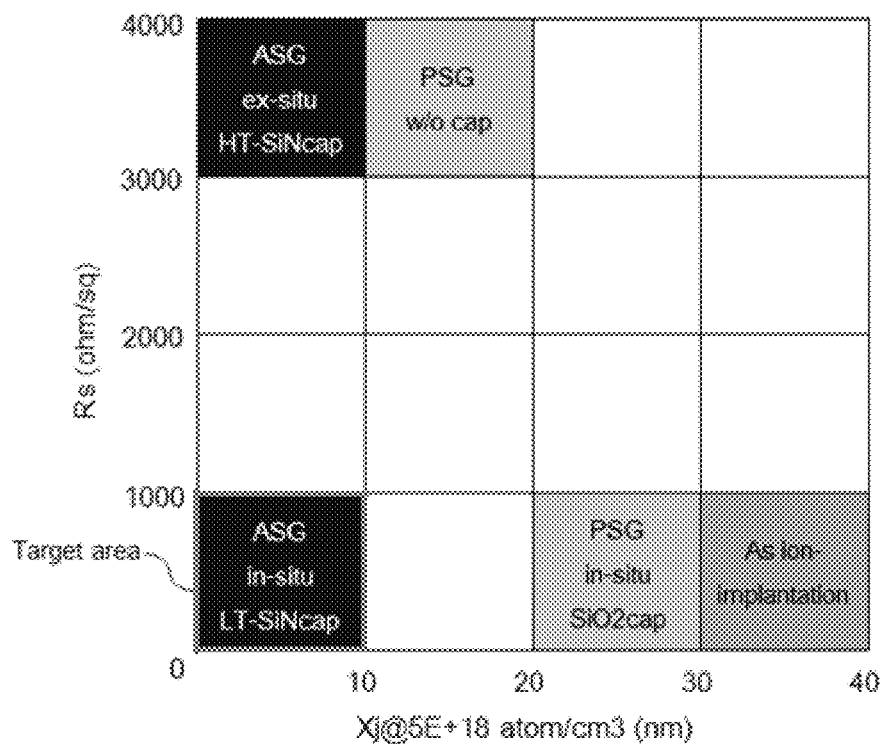


Fig. 5



1

METHOD FOR FORMING FILM HAVING LOW RESISTANCE AND SHALLOW JUNCTION DEPTH

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a method for forming on a substrate an arsenosilicate glass (ASG or AsSG) film with a cap film.

2. Related Art

Metal-oxide-semiconductor field effect transistors (MOSFETs) are fundamental switching devices to perform logic operations in large scale integrated circuits (LSIs). As the downsizing of MOSFETs progress, decrease in junction depth (X_j) and increase in doping concentration are indispensable in the scaling trend. FinFETs and Tri-gate FETs have fin structures for source/drain extension, and such devices require reduction of lateral resistance (or sheet resistance) of the source/drain extension regions to obtain larger drain current by scaling down of MOSFETs. Therefore, both shallow X_j (X_j is defined as the depth where dopant concentration is $5 \times 10^{18}/\text{cm}^3$) and low sheet resistance (R_s) of the source/drain extension regions are indispensable for further scaling down of MOSFETs. However, reducing R_s at shallow regions (e.g., $X_j < 10$ nm) has not been successful. The above characteristics also are important to turn-on voltage-modulation by Ground-Plane (GP) technique for Tunnel Field-Effect Transistor (TFET).

Any discussion of problems and solutions in relation to the related art has been included in this disclosure solely for the purposes of providing a context for the present invention, and should not be taken as an admission that any or all of the discussion was known at the time the invention was made.

SUMMARY OF THE INVENTION

Some embodiments provide a method for providing a thin film having a sheet resistance (R_s) of less than 1,000 ohm/sq with a junction depth (X_j) of less than 10 nm (preferably, an R_s of less than 500 ohm/sq with an X_j of less than 5 nm). In some embodiments, an arsenosilicate glass (ASG) film using arsenic (As) as n-type dopant is used in combination with a SiN cap, wherein a surface of the ASG film is treated in situ with a particular gas before forming the SiN cap. In some embodiments, the gas used for treating the surface of the ASG film is a combination of nitrogen gas, silane gas, hydrogen gas, and a noble gas. In some embodiments, the SiN cap is formed by plasma-enhanced atomic layer deposition (PEALD). In some embodiments, the ASG film is formed using solid-state doping. In some embodiments, the doping method is suitable for extension-doping in FinFETs or ground-plane doping in TFETs. In accordance with further exemplary embodiments, a method of realizing an R_s of less than 1,000 ohm/sq with an X_j of less than 10 nm is provided.

For purposes of summarizing aspects of the invention and the advantages achieved over the related art, certain objects and advantages of the invention are described in this disclosure. Of course, it is to be understood that not necessarily all such objects or advantages may be achieved in accordance with any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

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Further aspects, features and advantages of this invention will become apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features of this invention will now be described with reference to the drawings of preferred embodiments which are intended to illustrate and not to limit the invention. The drawings are greatly simplified for illustrative purposes and are not necessarily to scale.

FIG. 1A is a schematic representation of a PEALD (plasma-enhanced atomic layer deposition) apparatus for depositing a dielectric film usable in an embodiment of the present invention.

FIG. 1B illustrates a schematic representation of switching flow of an inactive gas and flow of a precursor gas usable in an embodiment of the present invention.

FIG. 2 is a schematic representation of lamination processes (a) to (b), indicating schematic cross sections of a partially fabricated integrated circuit according to a comparative example.

FIG. 3 is a schematic representation of lamination processes (a) to (c), indicating schematic cross sections of a partially fabricated integrated circuit according to an embodiment of the present invention.

FIG. 4 is a graph showing a target area defined by sheet resistance (R_s) and junction depth (X_j) according to an embodiment of the present invention, in relation to those of comparative examples.

FIG. 5 is an illustrative representation of the graph of FIG. 4.

DETAILED DESCRIPTION OF EMBODIMENTS

In this disclosure, "gas" may include vaporized solid and/or liquid and may be constituted by a single gas or a mixture of gases. In this disclosure, a process gas introduced to a reaction chamber through a showerhead may be comprised of, consist essentially of, or consist of a silicon-containing gas and an additive gas. The silicon-containing gas and the additive gas can be introduced as a mixed gas or separately to a reaction space. The silicon-containing gas can be introduced with a carrier gas such as a noble gas. A gas other than the process gas, i.e., a gas introduced without passing through the showerhead, may be used for, e.g., sealing the reaction space, which includes a seal gas such as a noble gas. In some embodiments, "film" refers to a layer continuously extending in a direction perpendicular to a thickness direction substantially without pinholes to cover an entire target or concerned surface, or simply a layer covering a target or concerned surface. In some embodiments, "layer" refers to a structure having a certain thickness formed on a surface or a synonym of film or a non-film structure. A film or layer may be constituted by a discrete single film or layer having certain characteristics or multiple films or layers, and a boundary between adjacent films or layers may or may not be clear and may be established based on physical, chemical, and/or any other characteristics, formation processes or sequence, and/or functions or purposes of the adjacent films or layers.

Further, in this disclosure, the article "a" or "an" refers to a species or a genus including multiple species unless specified otherwise. The terms "constituted by" and "having" refer independently to "typically or broadly comprising", "comprising", "consisting essentially of", or "consisting of" in some embodiments. Also, in this disclosure, any

defined meanings do not necessarily exclude ordinary and customary meanings in some embodiments.

Additionally, in this disclosure, any two numbers of a variable can constitute a workable range of the variable as the workable range can be determined based on routine work, and any ranges indicated may include or exclude the endpoints. Additionally, any values of variables indicated (regardless of whether they are indicated with "about" or not) may refer to precise values or approximate values and include equivalents, and may refer to average, median, representative, majority, etc. in some embodiments.

In the present disclosure where conditions and/or structures are not specified, the skilled artisan in the art can readily provide such conditions and/or structures, in view of the present disclosure, as a matter of routine experimentation. In all of the disclosed embodiments, any element used in an embodiment can be replaced with any elements equivalent thereto, including those explicitly, necessarily, or inherently disclosed herein, for the intended purposes. Further, the present invention can equally be applied to apparatuses and methods.

The embodiments will be explained with respect to preferred embodiments. However, the present invention is not limited to the preferred embodiments.

In some embodiments, a method for forming on a substrate a doped silicon oxide film with a cap film, comprises: (i) forming an arsenosilicate glass (ASG) film as an arsenic (As)-doped silicon oxide film on a substrate; (ii) continuously treating a surface of the ASG film with a treating gas constituted by Si, N, and H without excitation; and (iii) continuously forming a silicon nitride (SiN) film as a cap film on the treated surface of the ASG film. By using the ASG film, in place of phosphorus-doped silicon dioxide glass (PSG) film, in combination with the SiN cap in place of a SiO cap, and treating in situ a surface of the ASG film with the treating gas prior to depositing the SiN cap thereon, a structure where a sheet resistance (R_s) is as low as 1,000 ohm/sq (preferably 500 ohm/sq or less), and a junction depth (X_j) (as the depth of $5E+18$ atom/cm³) is as small as 10 nm (preferably 5 nm or less) can be fabricated, indicating that the concentration of dopant (As) is high only in a top surface of the substrate at the interface (i.e., high concentration and shallow diffusion of dopant into the substrate). In some embodiments, the in-film concentration of As in the ASG film is approximately $1E+22$ atom/cm³. Conventionally, it was not successful to reduce R_s when X_j was as small as 10 nm. Arsenic does not diffuse as much in a silicon substrate as does phosphorus, thereby contributing to a small junction depth, and also, the SiN cap blocks diffusion of As more than does a SiO cap if the interface is not exposed to air, thereby contributing to higher concentration of As on the substrate side than the cap side. Without being limited by the theory, as a result, both a low R_s and a low X_j can be achieved according to some embodiments. In this disclosure, the "ASG" film and "SiN" film can contain impurities including unavoidable elements to the extent accepted by one of ordinary skill in the art as an "ASG" film and "SiN" film, respectively. In some embodiments, the substrate is a silicon wafer or has an underlying semiconductor layer such as a silicon layer.

In some embodiments, a sheet resistance (R_s) and an As junction depth (X_j) at an interface between the ASG film and the substrate after an annealing step are approximately 500 ohm/sq or less (e.g., 100 ohm/sq to 400 ohm/sq), and approximately 5 nm or less (e.g., 1 nm to 4 nm), respectively.

In this disclosure, the word "continuously" refers to at least one of the following: without breaking a vacuum, without being exposed to air, without opening a chamber, as an in-situ process, without interruption as a step in sequence, without changing process conditions, and without causing chemical changes on a substrate surface between steps, depending on the embodiment. In some embodiments, an auxiliary step such as purging or other negligible step in the context does not count as a step, and thus, the word "continuously" does not exclude being intervened with the auxiliary step. By continuously conducting steps (i) through step (iii), the surface of the ASG film is treated with the treating gas fully without being exposed to air or any other oxygen-containing atmosphere throughout steps (i) to (iii), so that the high concentration of dopant can be maintained in the ASG film. In some embodiments, steps (i) to (iii) are conducted in a same reaction chamber. Accordingly, productivity can significantly be improved. Since step (ii) is conducted without exciting gases, substantially no film is formed on the surface of the ASG film, but gases are adsorbed on the surface of the ASG film. By way of step (ii), the interface between the ASG film and the SiN cap can effectively block diffusion or migration of As from the ASG film toward the SiN cap. A combination of Si, N, and H included in the treating gas is effective because these gases can be used for SiN cap formation and their flow can fully be stabilized before the SiN cap formation starts.

In some embodiments, all the gases including the treatment gas used in step (ii) are identical to all the gases used in step (iii), so that step (ii) and step (iii) can continuously be conducted without any interruption or any intervention therebetween, thereby not only increasing productivity but also forming the SiN cap layer having a more effective interface for blocking diffusion of the dopant. In some embodiments, all the gases including the treatment gas used in step (ii) are identical to all the gases used in step (iii) not only in kind but also in quantity (flow rate). In some embodiments, in step (ii), the treating gas is supplied with a noble gas such as helium (He), neon (Ne), argon (Ar), krypton (Kr), and/or xenon (Xe). In some embodiments, the treating gas in step (ii) comprises N₂ gas, SiH₄ gas, and H₂ gas, or other silicon-containing gas such as Si₂H₆ and other nitrogen- and hydrogen-containing gas such as NH₃. Due to the surface treatment, gas feeds for the SiN cap formation can effectively be stabilized before starting the SiN cap formation, and changing the recipe for the SiN cap formation (mainly changing the setting of a plasma generator) can smoothly be accomplished.

In some embodiments, the concentration of As in the ASG film is approximately $1E+22$ atom/cm³, and the thickness of the ASG film formed in step (i) is approximately 5 nm or less (typically 0.5 nm to 5 nm).

In some embodiments, in step (i), the ASG film is formed by atomic layer deposition (ALD) with solid-state doping. In some embodiments, the solid-state doping is conducted at a temperature of approximately 300° C. or lower. In some embodiments, the ALD is a plasma-enhanced ALD. In some embodiments, the solid-state doping is conducted based on the disclosure of U.S. Patent Application Publication No. 2013/0115763, the disclosure of which is herein incorporated by reference in its entirety. Any suitable method of forming an ASG film, including any conventional methods such as plasma doping, ion-assisted deposition and doping (IADD), spin-on coating, sub-atmospheric pressure chemical vapour deposition (SACVD), or ALD, can be used in some embodiments.

In some embodiments, the thickness of the SiN film formed in step (iii) is approximately 5 nm or less (typically 0.5 nm to 5 nm). In some embodiments, the SiN film is deposited by atomic layer deposition (ALD). In some embodiments, the ALD is a plasma-enhanced ALD. Any suitable method of forming a SiN cap, including any conventional methods such as low-pressure CVD or PEALD (such as U.S. Patent Application Publication No. 2014/0141625 and No. 2013/0330933, each disclosure of which is herein incorporated by reference in its entirety), can be used in some embodiments.

In some embodiments, the method further comprises, after step (iii), annealing the SiN film formed on the ASG film. In this disclosure, "annealing" refers to a process which dopant such as phosphorous or arsenic is diffused into the silicon substrate.

In some embodiments, the ASG film may be formed as a solid-state doping (SSD) layer by PEALD, one cycle of which is conducted under conditions shown in Table 1 below.

TABLE 1

(the numbers are approximate) Conditions for ASG Film Deposition	
Substrate temperature	50 to 400° C. (preferably 100 to 300° C.)
Pressure	133 to 800 Pa (preferably 200 to 600 Pa)
Silicon precursor	Silicon-containing precursor such as bis(diethylamino)silane (BDEAS),
Silicon precursor pulse	0.05 to 5.0 sec (preferably 0.2 to 1.0 sec)
Silicon precursor purge	0.1 to 10.0 sec (preferably 0.3 to 1.0 sec)
Dopant precursor	Arsenic-containing precursor such as arsenic trioxide
Dopant precursor pulse	0.05 to 5.0 sec (preferably 0.1 to 3, or 0.2 to 1.0 sec)
Dopant precursor purge	0.1 to 10.0 sec (preferably 0.3 to 5, or 0.3 to 1.0 sec)
Reactant	Oxidizing gas such as oxygen, ozone
Flow rate of reactant (continuous)	10 to 4000 sccm (preferably 1000 to 2000 sccm)
Dilution gas (rare gas)	He, Ar
Flow rate of dilution gas (continuous)	100 to 6000 sccm (preferably 2000 to 4000 sccm)
RF power (13.56 MHz) for a 300-mm wafer	10 to 1,000 W (preferably 30 to 500 W)
RF power pulse	0.1 to 10 sec (preferably 0.1 to 5 sec)
Purge upon the RF power pulse	0.1 to 10 sec (preferably 0.05 to 4 sec)
Thickness of film	0.5 to 10 nm (preferably 0.5 to 5 nm)

The dopant precursor may be provided with the aid of a carrier gas. Since ALD is a self-limiting adsorption reaction process, the number of deposited precursor molecules is determined by the number of reactive surface sites and is independent of the precursor exposure after saturation, and a supply of the precursor is such that the reactive surface sites are saturated thereby per cycle.

In some embodiments, an arsenosilicate glass ALD cycle comprises a silicon phase, a dopant phase and an oxidation phase. The silicon phase comprises providing a pulse of BDEAS to a reaction chamber comprising a substrate. Excess BDEAS is removed and the substrate is contacted with a pulse of a dopant precursor in the dopant phase. Excess dopant precursor and reaction by-products, if any, are removed. The substrate is then contacted with oxygen plasma to form a boron or phosphorous-arsenosilicate glass. The oxygen plasma may be generated in situ, for example in an oxygen gas that flows continuously throughout the ALD

cycle. In other embodiments the oxygen plasma may be generated remotely and provided to the reaction chamber.

As mentioned above, each pulse or phase of each ALD cycle is preferably self-limiting. An excess of reactants is supplied in each phase to saturate the susceptible structure surfaces. Surface saturation ensures reactant occupation of all available reactive sites (subject, for example, to physical size or "steric hindrance" restraints) and thus ensures excellent step coverage. In some embodiments the pulse time of one or more of the reactants can be reduced such that complete saturation is not achieved and less than a monolayer is adsorbed on the substrate surface. However, in some embodiments the dopant precursor step is not self-limiting, for example, due to decomposition or gas phase reactions.

In some embodiments, the silicon precursor and the dopant precursor are both provided prior to any purge step. Thus, in some embodiments a pulse of silicon precursor is provided, a pulse of dopant precursor is provided, and any unreacted silicon and dopant precursor is purged from the reaction space. The silicon precursor and the dopant precursor may be provided sequentially, beginning with either the silicon precursor or the dopant precursor, or together. In some embodiments, the silicon precursor and dopant precursor are provided simultaneously. The ratio of the dopant precursor to the silicon precursor may be selected to obtain a desired concentration of dopant in the deposited thin film.

The ratio of silicon precursor cycles to dopant precursor cycles may be selected to control the dopant concentration in the ultimate film deposited by the PEALD process. For example, for a low dopant density, the ratio of dopant precursor cycles to silicon precursor cycles may be on the order of 1:10. For a higher concentration of dopant, the ratio may range up to about 1:1 or higher such as 1.5:1, 2:1, 2.5:1, 3:1, 4:1, etc. In some embodiments all of the deposition cycles in an ALD process may be dopant precursor cycles. The ratio of deposition cycles comprising dopant to deposition cycles that do not include dopant (such as the ratio of dopant precursor cycles to silicon precursor cycles, or the ratio of dopant oxide cycles to silicon precursor cycles) may be referred to as the control knob. For example, if one dopant precursor cycle is provided for every four silicon precursor cycles, the control knob is 0.25. If no undoped oxide cycles are used, the control knob may be considered to be infinite.

By controlling the ratio of dopant precursor cycle to silicon precursor cycle, the dopant concentration can be controlled from a density range of about 0 atoms of dopant to about $5E+22/cm^3$ atoms of dopant. Density may be measured, for example, by SIMS (secondary-ion-probe mass spectrometry).

In addition, the dopant density can be varied across the thickness of the film by changing the ratio of dopant precursor cycles to silicon precursor cycles during the deposition process. For example, a high density of dopant may be provided near the substrate surface (lower ratio of silicon precursor cycles to dopant precursor cycle), such as near a Si surface and the density of dopant at the top surface away from the substrate may be low (higher ratio of silicon precursor cycles to dopant precursor cycles). In other embodiments a high density of dopant may be provided at the top surface with a lower density near the substrate surface.

In some embodiments, an arsenosilicate glass layer is formed by providing a dopant precursor cycle at certain

intervals in a silicon oxide deposition process. The interval may be based, for example, on cycle number or thickness. For example, one or more dopant precursor deposition cycles may be provided after each set of a predetermined number of silicon precursor deposition cycles, such as after every 10, 20, 50, 100, 200, 500 etc. cycles. In some embodiments, undoped silicon oxide deposition cycles may be repeated until a silicon oxide layer of a predetermined thickness is reached, at which point one or more dopant precursor cycles are then carried out. This process is repeated such that dopant is incorporated in the film at specific thickness intervals. For example, one or more dopant precursor cycles may be provided after each 5 nm of undoped SiO₂ that is deposited. The process is then repeated until an arsenosilicate glass thin film of a desired thickness and composition has been deposited.

In some embodiments in an ALD process for producing arsenosilicate glass films, one or more “dopant oxide” deposition cycles are provided along with undoped silicon oxide deposition cycles. The process may also include one or more arsenosilicate glass deposition cycles.

In the “dopant oxide” deposition cycles, the silicon precursor is omitted from the arsenosilicate glass deposition cycles described above. Thus, the substrate is exposed to alternating and sequential pulses of dopant precursor and an oxidant, such as oxygen plasma. Other reactive oxygen sources may be used in some embodiments. In some embodiments, an arsenosilicate glass film is provided by conducting multiple dopant oxide deposition cycles and multiple silicon oxide deposition cycles. The ratio of dopant oxide cycles to silicon precursor cycles may be selected to control the dopant concentration in the ultimate arsenosilicate glass film. For example, for a low dopant density, the ratio of dopant oxide cycles to silicon precursor cycles may be on the order of 1:10. In other embodiments a high dopant density is achieved by increasing the ratio of dopant oxide cycles to silicon precursor cycles to 1:1 or even higher, such as 1.5:1, 2:1, 2.5:1, 3:1, 4:1 etc. For example, for a high dopant density, such as a high B density, the ratio of dopant oxide cycles to silicon precursor cycles may be on the order of 6:1, or even 10:1.

The density can be varied across the thickness of the film by changing the ratio of dopant oxide cycles to silicon oxide cycles during the deposition process. For example, a high density of dopant may be provided near the substrate surface by using a lower ratio of silicon oxide cycles to dopant oxide cycles and the density of dopant at the top surface may be lower by providing a higher ratio of silicon oxide cycles to dopant oxide cycles.

In some embodiments, an in-situ plasma pre-treatment of the substrate is conducted before SSD layer deposition to enhance doping efficiency into the Si fin. For example, H₂ plasma pre-treatment can provide some tuning space for FinFET device design. The pre-treatment is not limited only H₂ plasma. In some embodiments, the pre-treatment plasma may be selected from Ar, He, H₂, fluorine-containing gas, and their mixed gas plasma.

In some embodiments, the ALD cycle disclosed in U.S. Patent Application Publication No. 2013/0115763, the disclosure of which is incorporated by reference in its entirety, can be employed for the ASG film (referred to also as “dopant layer”).

In some embodiments, the dopant layer is treated with a treating gas under conditions shown in Table 2 below.

TABLE 2

(the numbers are approximate) Conditions for Surface Treatment	
5 Susceptor temperature	100 to 550° C. (preferably 200 to 300° C.) (the temperature of the wall is typically about 130° C., and the temperature of the showerhead is typically about 150° C.)
Pressure	50 to 1,000 Pa (preferably 200 to 400 Pa)
Si-containing gas	SiH ₄ , Si ₂ H ₆
10 Flow rate of Si-containing gas (continuous)	10 to 500 sccm (preferably 50 to 400 sccm)
N-containing gas	N ₂
Flow rate of N-containing gas (continuous)	250 to 3,000 sccm (preferably 500 to 1500 sccm)
H-containing gas	H ₂ , NH ₃
15 Flow rate of H-containing gas (continuous)	100 to 2,000 sccm (preferably 250 to 500 sccm)
Alternatively, N/H-containing gas (continuous)	NH ₃ , N ₂ H ₂
Flow rate of N/H-containing gas (continuous)	100 to 2,000 sccm (preferably 250 to 500 sccm)
Ratio of Si/N/H	2/(5-20)/(3-10) (preferably 2/(8-12)/(3-8))
20 Dilution gas	Inert gas such as Ar, He, N ₂
Flow rate of dilution gas (continuous)	Ar: 0 to 2,000 sccm (preferably 0 to 1000 sccm); He: 0 to 2,000 sccm (preferably 0 to 1000 sccm)
Seal gas	Noble gas such as He (about 200 sccm)
25 Duration of Treatment	1 to 30 sec (preferably 10 to 20 sec)

Although the surface treatment is continuously conducted after completion of the ALD cycle, the surface treatment is not conducted as a part of the ASG film formation, but is a discrete step which is distinguished from the ASG film formation, i.e., the surface treatment is initiated after the ASG film formation is completely finished. For example, the surface treatment is not any part of ALD cycles for the ASG film and is initiated after purging upon completion of the ALD cycles (which purging is conducted using, e.g., a noble gas as such as Ar at a flow rate of 950 to 2,000 sccm for 3 to 60 seconds to remove O₂ used in the ASG film formation prior to feeding SiH₄ used in the surface treatment). Further, although the SiN cap formation is continuously conducted after completion of the surface treatment, the surface treatment is not conducted as a part of the SiN cap formation, i.e., the surface treatment is not initiated as a start-up step of the SiN cap formation although the SiN cap formation is continuously conducted upon the surface treatment (without any intervening step including purging). For example, the surface treatment is not any part of ALD cycles for the SiN cap. However, in some embodiments, gases which are the same as those used in the ALD cycles for the SiN cap can be used for the surface treatment. Further, in some embodiments, the flow rates of these gases in the surface treatment can be the same as those for the ALD cycles for the SiN cap. In some embodiments, continuously fed gas such as dilution gas in the surface treatment can be continuously fed to the reaction space for the ALD cycles for the SiN cap after completion of the surface treatment without interruption. Alternatively, in some embodiments, at least some conditions for the surface treatment can be different from those for the ALD cycles for the SiN cap.

By avoiding exposure of the surface of the dopant layer to air or other oxygen-containing atmosphere, and by exposing the surface to a Si/N/H gas (i.e., a gas constituted by Si, N, and H), when the surface is covered with a cap layer, loss of dopant from the dopant layer can effectively be inhibited. Since the gases are not excited, the gases are adsorbed on the surface in a manner of chemisorption, typically, no film is formed on the surface of the dopant layer, but a layer similar

to an atomic layer may be formed on the surface. The ratio of Si/N/H (i.e., the ratio of Si-containing gas/N-containing gas/H-containing gas) may be in a range of 2/(5-20)/(3-10) (Si<H<N), typically 2/10/5. Additionally, if the duration of the surface treatment is shorter than 3 seconds, whereas if the duration of the surface treatment is longer than 20 seconds.

Upon the surface treatment of the surface of the dopant layer, a SiN cap layer is continuously formed without being exposed to air or other oxygen-containing atmosphere. In some embodiments, the SiN cap layer may be formed by cyclic CVD or PEALD, one cycle of which cyclic CVD is conducted under conditions shown in Table 3 below. In cyclic CVD, a precursor for a SiN cap layer is typically pulsed while other gases and RF power are continuously charged; however, in place of or in addition to the precursor flow, RF power and any of the other gases can be pulsed as long as plasma reaction can occur in the reaction space, rather than on the substrate surface as in ALD. In some embodiments, the pressure of the reaction space is substantially constant while conducting cyclic CVD, wherein the pressure can be maintained by, e.g., switching precursor flow and inactive gas flow while continuously feeding the precursor and the inactive gas using a gas flow system illustrated in FIG. 1B which is explained later.

TABLE 3

(the numbers are approximate) Conditions for SiN Cap Formation (cyclic CVD)	
Substrate temperature	100 to 550° C. (preferably 200 to 300° C.) (the temperature of the wall is typically about 130° C., and the temperature of the showerhead is typically about 150° C.)
Pressure	50 to 1,000 Pa (preferably 200 to 400 Pa)
Silicon precursor	Silicon-containing precursor such as SiH ₄ , Si ₂ H ₆ .
Silicon precursor pulse	0.05 to 5.0 sec (preferably 0.1 to 3)
Reactant	Nitridizing gas such as nitrogen gas, NH ₃
Flow rate of reactant (continuous)	10 to 2000 sccm (preferably 50 to 1000 sccm)
Dilution gas (rare gas)	He, Ar
Flow rate of dilution gas (continuous)	100 to 6000 sccm (preferably 1000 to 5000 sccm)
RF power (13.56 MHz) for a 300-mm wafer (continuous)	10 to 1,000 W (preferably 20 to 500 W)
Thickness of film	0.5 to 10 nm (preferably 0.5 to 5 nm)

In some embodiments, the SiN cap formation can be accomplished by PEALD under conditions similar to those indicated in Table 3 except that purging (e.g., 0.1 to 10.0 seconds, preferably 0.3 to 5 seconds) is conducted after the silicon precursor pulse, RF power is pulsed (e.g., 0.1 to 10 seconds, preferably 0.5 to 5 seconds), and after the RF power pulse, purging is conducted (e.g., 0.1 to 10 seconds, preferably 0.1 to 4 seconds).

In some embodiments, the gases and their flow rates used for the SiN cap formation are identical to those used for the surface treatment, and the SiN cap formation can be continuously conducted upon completion of the surface treatment. In some embodiments, Ar is used as a purge gas and continuously flows through its supply line, thereby flowing into the reaction space when the silicon precursor is not fed to the reaction space or flowing into a vent line when the silicon precursor is fed to the reaction space by valve switching. In some embodiments, the purge gas is Ar at a flow rate of about 950 sccm to about 2,000 sccm.

In some embodiments, the cap layer is directly over and contacting the dopant layer which has been treated with a

treating gas. The cap layer is constituted by SiN. Since the surface of the dopant layer is covered with the SiN cap layer without being exposed to air, the SiN cap layer can effectively maintain As concentration in the dopant layer even if the thickness of the SiN cap layer is small such as less than 2 nm in some embodiments.

In some embodiments, the ALD cycle disclosed in U.S. Patent Application Publication No. 2013/0115763, the disclosure of which is incorporated by reference in its entirety, can be employed for the cap layer.

In some embodiments, after depositing the cap layer, the substrate is subjected to annealing to diffuse As into substrate. In some embodiments, the annealing may be conducted under conditions shown in Table 4 below.

TABLE 4

(the numbers are approximate) Conditions for Annealing	
Substrate temperature	600 to 1500° C. (preferably 900 to 1100° C.)
Pressure	101325 Pa
Atmosphere	N ₂ , H ₂
Duration of annealing	1 to 120 sec (preferably 1 to 60 sec)

The embodiments will be explained with respect to preferred embodiments. However, the present invention is not limited to the preferred embodiments.

FIG. 1A is a schematic view of a PEALD apparatus, desirably in conjunction with controls programmed to conduct the sequences described below, usable in some embodiments of the present invention. In this figure, by providing a pair of electrically conductive flat-plate electrodes 4, 2 in parallel and facing each other in the interior 11 of a reaction chamber 3, applying HRF power (13.56 MHz or 27 MHz) 5 and LRF power of 5 MHz or less (400 kHz~500 kHz) 50 to one side, and electrically grounding 12 to the other side, a plasma is excited between the electrodes. A temperature regulator is provided in a lower stage 2 (the lower electrode), and a temperature of a substrate 1 placed thereon is kept constant at a given temperature. The upper electrode 4 serves as a shower plate as well, and reaction gas and rare gas are introduced into the reaction chamber 3 through a gas flow controller 23, a pulse flow control valve 31, and the shower plate. Additionally, in the reaction chamber 3, an exhaust pipe 6 is provided, through which gas in the interior 11 of the reaction chamber 3 is exhausted. Additionally, the reaction chamber is provided with a seal gas flow controller 24 to introduce seal gas into the interior 11 of the reaction chamber 3 (a separation plate for separating a reaction zone and a transfer zone in the interior of the reaction chamber is omitted from this figure). In some embodiments, the deposition of ASG film, surface treatment, and deposition of SiN cap are performed in the same apparatus such as that described above, so that all the steps can continuously be conducted without exposing the substrate to air or other oxygen-containing atmosphere. In some embodiments, a remote plasma unit can be used for exciting a gas.

In some embodiments, in the apparatus depicted in FIG. 1A, in place of the pulse flow control valve 31, a system of switching flow of an inactive gas and flow of a precursor gas can be used. FIG. 1B illustrates a schematic representation of such a switching flow system. In (a) in FIG. 1B, valves V1 (X) and V2 (R) are closed, and valves V1 (R) and V2 (X) are open, so that a precursor gas flows to a vent via valve V1 (R), and an inactive gas flows to a reactor via valve V2 (X). In (b) in FIG. 1B, by simultaneously closing valves V1 (R) and V2 (X) and opening valves V1 (X) and V2 (R), the

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precursor gas is instantly directed to flow to the reactor, and the inactive gas is instantly directed to flow to the vent, without substantial changes in the flow rate while maintaining continuous flows. The vent can be set downstream of an exhaust, for example.

In some embodiments, the surface treatment can be continuously conducted in a chamber different from the chamber used for the deposition of ASG film using a cluster apparatus (a substrate is transferred between chambers via a wafer-handling chamber without being exposed to air).

A skilled artisan will appreciate that the apparatus includes one or more controller(s) (not shown) programmed or otherwise configured to cause the deposition and reactor cleaning processes described elsewhere herein to be conducted. The controller(s) are communicated with the various power sources, heating systems, pumps, robotics and gas flow controllers or valves of the reactor, as will be appreciated by the skilled artisan.

FIG. 2 is a schematic representation of lamination processes (a) to (b), indicating schematic cross sections of a partially fabricated integrated circuit according to a comparative example. In this example, an n-type doped film 21 is deposited on a Si substrate 22 in process (a), wherein the n-type dopant may be phosphorus. Thereafter, a SiO₂ cap film 23 is deposited on the surface of the n-type doped film 21 in process (b). Since phosphorus is used as n-type dopant, no surface treatment is conducted, and the SiO₂ cap film is used, high concentration of dopant with deep diffusion into the Si substrate is likely to occur. In contrast, FIG. 3 is a schematic representation of lamination processes (a) to (c), indicating schematic cross sections of a partially fabricated integrated circuit according to an embodiment of the present invention. In this embodiment, an n-type doped film 31 is deposited on a Si substrate 32 in process (a), wherein the n-type dopant is arsenic. Thereafter, the surface of the As-doped film 31 is treated in situ with a treating gas in process (b), thereby covering the surface with a chemisorbed treating gas 33. Thereafter, a SiN cap film 34 is deposited on the treated surface of the As-doped film 31 in process (c) (in the figure, "LT-SiN cap" refers to low-temperature SiN cap deposited by cyclic CVD or PEALD). Since arsenic is used as n-type dopant, surface treatment is conducted in situ, and the SiN cap film is formed in situ, high concentration of dopant with shallow diffusion into the Si substrate can occur (i.e., a low sheet resistance (Rs) and a low junction depth (Xj) are realized at the interface).

The present invention is further explained with reference to working examples below. However, the examples are not intended to limit the present invention. In the examples where conditions and/or structures are not specified, the skilled artisan in the art can readily provide such conditions and/or structures, in view of the present disclosure, as a matter of routine experimentation. Also, the numbers applied in the specific examples can be modified by a range of at least $\pm 50\%$ in some embodiments, and the numbers are approximate.

EXAMPLES

An arsenosilicate glass (ASG) film was formed on a Si substrate ($\Phi 300$ mm) by PEALD, one cycle of which was conducted under the conditions shown in Table 5 below using the PEALD apparatus illustrated in FIG. 1A (including a modification illustrated in FIG. 1B) with the sequence illustrated in FIG. 3.

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TABLE 5

(the numbers are approximate) Conditions for ASG Film Deposition	
5 Substrate temperature	300° C.
Pressure	400 Pa
Silicon precursor	bis(diethylamino)silane (BDEAS)
Silicon precursor pulse	0.3 sec
Silicon precursor purge	0.8 sec
Dopant precursor	Arsenic triethoxide
10 Dopant precursor pulse	0.3 sec
Dopant precursor purge	5.0 sec
Reactant	O ₂
Flow rate of reactant (continuous)	500 sccm
Dilution gas (rare gas)	Ar
15 Flow rate of dilution gas (continuous)	2200 sccm
RF power (13.56 MHz) for a 300-mm wafer	200 W
RF power pulse	0.4 sec
Purge upon the RF power pulse	0.1 sec
20 Thickness of film	5 nm

The dopant layer was treated in situ with a treating gas under conditions shown in Table 6 below in the same apparatus.

TABLE 6

(the numbers are approximate) Conditions for Surface Treatment	
30 Substrate temperature	300° C.
Pressure	300 Pa
Si-containing gas	SiH ₄
Flow rate of Si-containing gas (continuous)	200 sccm
N-containing gas	N ₂
35 Flow rate of N-containing gas (continuous)	1,000 sccm
H-containing gas	H ₂
Flow rate of H-containing gas (continuous)	500 sccm
Ratio of Si/N/H	2/10/5
40 Dilution gas (continuous)	Ar (1,800 sccm); He (1,500 sccm)
Duration of Treatment	20 sec

Thereafter, a SiN cap layer was formed in situ by cyclic CVD, one cycle of which was conducted under conditions shown in Table 7 below in the same apparatus (the gases and their flow rates were substantially the same as those for the surface treatment).

TABLE 7

(the numbers are approximate) Conditions for SiN Cap Formation	
50 Substrate temperature	300° C.
Pressure	300 Pa
Silicon precursor	SiH ₄
55 Silicon precursor pulse	0.2 sec
Reactant	H ₂ , N ₂
Flow rate of reactant (continuous)	H ₂ : 500 sccm; N ₂ : 1,000 sccm
Dilution gas (rare gas)	Ar, He
Flow rate of dilution gas (continuous)	Ar: 1,800 sccm; He: 1,500 sccm
Purge gas	Ar
60 Flow rate of purge gas (switching between precursor and purge gas)	1,800 sccm
RF power (13.56 MHz) (continuous) for a 300-mm wafer	35 W
Thickness of film	5 nm

After depositing the cap layer, the substrate was subjected to annealing to diffuse As into Si substrate under conditions shown in Table 8 below.

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TABLE 8

(the numbers are approximate) Conditions for Annealing	
Substrate temperature	1035.° C.
Pressure	101325 Pa
Atmosphere	He
Duration of annealing	1.5 sec

As comparative examples, the following structures were produced:

TABLE 9

Name in FIG. 4	Remarks
“▲SiO ₂ cap”	A SiO ₂ cap was formed by PEALD in place of the SiN cap of the example.
“▲HT-SiN cap”	A SiN cap was formed by LPCVD (at 690° C.) without the surface treatment of the example.
“●No cap”	No cap was formed on a PSG film formed in place of the ASG film of the example.
“●SiO ₂ cap”	A SiO ₂ cap was formed by PEALD in place of the SiN cap of the example, on a PSG film formed in place of the ASG film of the example.
“◇As I/I”	As was doped by ion implantation.

Upon the annealing, the obtained films were analyzed in terms of sheet resistance (Rs) and junction depth (Xj). The results are shown in Table 10 below. The results are also shown in FIG. 4. FIG. 4 is a graph showing a target area defined by sheet resistance (Rs) and junction depth (Xj) according to the example of the present invention, in relation to those of the comparative examples. The sheet resistance was measured using a CDE ResMAP 463 tool at 49 points on the substrate, and the junction depth was measured using an Atomika 4100 SIMS tool with a Cs primary beam.

TABLE 10

(the numbers are approximate)						
In FIG. 4	Dopant layer	Surface treatment	Cap	In-film conc. (atom/cm ³)	Xj @5E+18 (atom/cm ³)	Rs (ohm/sq)
▲ LT-SiN cap	ASG	Yes	LT-SiN 5 nm	1.0E+22	2.7	354
▲ SiO ₂ cap”	ASG	No	SiO ₂ 5 nm	1.0E+22	1.5	3206
▲ HT-SiN cap	ASG	No (air exposure)	HT-SiN 5 nm	1.0E+22	2.9	6732
● No cap	PSG	No	SiO ₂ 5 nm	6.0E+21	26.5	798
● SiO ₂ cap	PSG	No	No	6.0E+21	13.5	3276
◇ As I/I	N/A	N/A	N/A	N/A	40	312

As shown in Table 10 and FIG. 4, except for “LT-SiN cap” (an example of the invention), none of the other films satisfied an Rs of 1000 ohm/sq or less and an Xj of 10 nm or less. Even the film doped by As ion implantation did not satisfy the above criteria. Further, even though the ASG film was used, and the SiN cap was formed thereon (in “HT-SiN cap”), when the surface treatment was not conducted (in that case, in order to deposit the SiN cap by PLCVD, the substrate was transferred from the ALD chamber to the CVD chamber and was exposed to air for about 3600 seconds), although diffusion of dopant was shallow (Xj=2.9 nm), dopant concentration was low (Rs=6732 ohm/sq). Only “LT-SiN cap” satisfied high concentration of dopant (Rs=354) with shallow diffusion of dopant (Xj=2.7 nm). FIG. 5 is an illustrative representation of the graph of FIG.

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4. It is surprising that by forming on a Si substrate an ASG film which is surface-treated and then covered with a SiN cap (in-situ SiN cap), high concentration and shallow diffusion of dopant can be satisfied to the extent satisfying an Rs of less than 1000 ohm/sq and an Xj (depth of 5E+18) of less than 10 nm, more preferably an Rs of less than 500 ohm/sq and an Xj (depth of 5E+18) of less than 5 nm. The above properties are highly suitable for extension doping for FinFET devices, especially where the fin width is 10 nm (if dopant diffuses at a depth of 5 nm from both sides of the fin, the device will remain in an ON state, and will become non-functional).

It will be understood by those of skill in the art that numerous and various modifications can be made without departing from the spirit of the present invention. Therefore, it should be clearly understood that the forms of the present invention are illustrative only and are not intended to limit the scope of the present invention.

We Claim:

1. A method for forming on a substrate a doped silicon oxide film with a cap film, comprising:
 - (i) forming an arsenosilicate glass (ASG) film having a desired thickness as an arsenic (As)-doped silicon oxide film on a substrate;
 - (ii) after completion of step (i), continuously treating a surface of the ASG film with a treating gas constituted by Si, N, and H without excitation of the treating gas so as to adsorb the treating gas on the surface of the ASG film; and
 - (iii) after completion of step (ii), continuously forming a silicon nitride (SiN) film as a cap film on the treating gas-adsorbed surface of the ASG film.

2. The method according to claim 1, wherein all the gases including the treating gas used in step (ii) are identical to all the gases used in step (iii).

3. The method according to claim 1 wherein in step (ii), the treating gas is supplied with a noble gas.

4. The method according to claim 1, wherein the treating gas comprises N₂ gas, SiH₄ gas, and H₂ gas.

5. The method according to claim 1, wherein step (ii) is conducted at a temperature of 100° C. to 300° C.

6. The method according to claim 1, wherein the concentration of As in the ASG film is approximately 1E+22 atom/cm³.

7. The method according to claim 1, wherein the thickness of the ASG film formed in step (i) is approximately 5 nm or less.

8. The method according to claim 1, wherein in step (i), the ASG film is formed by atomic layer deposition (ALD) with solid-state doping.

9. The method according to claim 8, wherein the solid-state doping is conducted at a temperature of approximately 300° C. or lower.

10. The method according to claim 8, wherein the ALD is a plasma-enhanced ALD.

11. The method according to claim 1, wherein the thickness of the SiN film formed in step (iii) is approximately 5 nm or less.

12. The method according to claim 1, wherein the substrate is a silicon wafer.

13. The method according to claim 1, wherein the SiN film is deposited by cyclic CVD.

14. The method according to claim 13, wherein the cyclic CVD comprises feeding a precursor for the SiN film in pulses to a reaction space while maintaining pressure of the reaction space.

15. The method according to claim 1, further comprising, after step (iii), annealing the SiN film formed on the ASG film.

16. The method according to claim 15, wherein a sheet resistance (R_s) and an As-junction depth (X_j) of $5E+18$ atom/cm³ at an interface between the ASG film and the substrate after the annealing step are approximately 500 ohm/sq or less, and approximately 5 nm or less, respectively.

17. The method according to claim 15, wherein the in-film concentration of As in the ASG film is approximately $1E+22$ atom/cm³.

18. The method according to claim 1, wherein steps (i) to (iii) are conducted in a same reaction chamber.

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